

COMPLEXES OF RUTHENIUM(II) AND RUTHENIUM(III) WITH TERTIARY ARSINES

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Abstract—Ruthenium trichloride reacts with stoichiometric amounts of tertiary arsines in boiling ethanol to give paramagnetic complexes, $\text{RuCl}_3(\text{Ph}_2\text{RAs})_3$ (R = Me, Et, Pr, Bu), which react further with 2,2'-bipyridyl(bipy) and *o*-phenanthroline(phen) to yield brick red crystalline products, $\text{RuCl}_3(\text{N-N})(\text{Ph}_2\text{RAs})$ (N-N = bipy, phen). In the presence of excess arsine Ru(III) is reduced to Ru(II), and trichloro-bridged complexes of the formula $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6]\text{Cl}$ are formed. These on treatment with carbonylated solutions of rhodium chloride produce yellow crystals of $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6][\text{RhCl}_2(\text{CO})_2]$ containing Ru(II) and Rh(I). Several dicarbonyl complexes *cis*- $\text{RuX}_2(\text{CO})_2(\text{Ph}_2\text{RAs})_2$ (X = Cl, Br; R = Pr, Bu) have also been isolated.

INTRODUCTION

Ruthenium(III) halides are known to take part in a variety of reactions with tertiary phosphines and arsines in polar solvents[1-3]. The products may be simple octahedral adducts, of the type RuX_3L_3 , or compounds of the type $\text{RuX}_3\text{L}_2\text{S}$ (X = halogen; L = tertiary phosphine or arsine; S = solvent molecule). Further, it is quite common for ruthenium(III) to be reduced to ruthenium(II) (the polar solvent or the tertiary phosphine or arsine acting as the reducing agent) and give rise to complexes of the formulae RuX_2L_4 and RuX_2L_3 . But, very often halo-bridged binuclear complexes of composition $[\text{Ru}_2\text{X}_3\text{L}_6]\text{X}$ are obtained[4]. Trichloro-bridged complexes containing two different metal atoms, one of them being ruthenium(II) have also been isolated[5]. The reasons for this varied behaviour are not clearly understood.

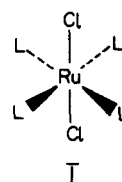
In an earlier communication[6] we have reported the reactions of ruthenium trichloride with the tertiary arsines (L), Ph_2MeAs and Ph_2EtAs , to form complexes of the formulae RuCl_2L_4 , $\text{RuCl}_2(\text{CO})\text{L}_3$, $\text{RuCl}_2(\text{CO})_2\text{L}_2$, $[\text{Ru}_2\text{Cl}_3\text{L}_6]\text{Y}$ (Y = Cl, ClO_4^- , BF_4^- , BPh_4^-) and RuCl_3L_3 . We report, here, the details of these investigations and their extension to the arsines Ph_2PrAs and Ph_2BuAs . We have also investigated the reactions of complexes of the type RuCl_3L_3 with the bidentate heterocyclic nitrogen bases, 2,2'-bipyridyl(bipy) and *o*-phenanthroline (phen).

RESULTS AND DISCUSSION

Ruthenium trichloride reacts in alcoholic solution with the simple arsines of the type Ph_2RAs (R = Me, Et, Pr, Bu), in the mole ratio 1:3, to give paramagnetic nonionic complexes of the formula $\text{RuCl}_3(\text{Ph}_2\text{RAs})_3$. We have reported earlier[6] that if the metal halide to arsine ratio is 1:6, a binuclear cationic complex of ruthenium(II) of the composition $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{EtAs})_6]\text{Cl}$ may be isolated. We now find that better results are obtained if the ratio is 1:8, and in this way analogous complexes with the arsines Ph_2MeAs , Ph_2PrAs and Ph_2BuAs have been synthesised. In the case of diphenyl methyl arsine a neutral complex of formula $\text{RuCl}_2(\text{Ph}_2\text{MeAs})_4$ is precipitated from the reaction mixture and the ionic complex $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{MeAs})_6]\text{Cl}$ can be isolated by concentrating the filtrate. Complexes of the type $\text{RuCl}_2(\text{Ph}_2\text{RAs})_4$ could not be isolated in the case of the higher arsines presu-

mably because of the higher solubility of these species and their ready conversion to the more stable binuclear cationic species. With diphenyl methyl arsine also, the compound, $\text{RuCl}_2(\text{Ph}_2\text{MeAs})_4$, that separates initially, dissolves very slowly in alcohol on refluxing with a small amount of the arsine, is converted to the binuclear complex cation. Further all the binuclear complexes react with NaY ($\text{Y}^- = \text{ClO}_4^-$, BF_4^- , BPh_4^-) in alcohol to give crystalline precipitates of $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6]\text{Y}$.

Magnetic susceptibility, conductivity and analytical results support the formulae assigned to these complexes. The complex $\text{RuCl}_2(\text{Ph}_2\text{MeAs})_4$ shows a single

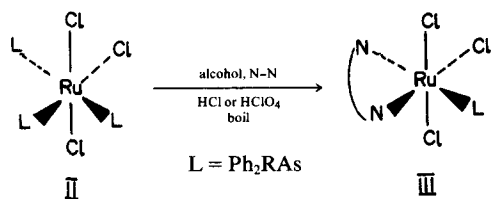


methyl resonance signal at 8.33 τ in the pmr spectrum indicating the equivalence of all the Ph_2MeAs ligands and so probably has the configuration I (L = Ph_2MeAs). The binuclear cationic complexes $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6]\text{Cl}$ also react with alcoholic solutions of carbonylated rhodium trichloride to give new complexes of the type $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6][\text{RhCl}_2(\text{CO})_2]$ containing Ru(II) in the cation and Rh(I) in the anion. These products behave as 1:1 electrolytes in nitrobenzene, and show two strong νCO bands in the 2000 cm^{-1} (Table 2) region of the IR, as is typical of *cis* carbonyl groups. The compounds are obviously formed by the displacement of the Cl^- in $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6]^+[\text{Cl}]^-$ by the bulky anion[7] $[\text{RhCl}_2(\text{CO})_2]^-$ present in the carbonylated solution of rhodium trichloride[8].

We have reported[9] recently that trihalo complexes of rhodium of the formula $\text{RhX}_3(\text{Ph}_2\text{RAs})_3$ undergo facile substitution reactions with the potentially bidentate nitrogen donor ligands bipy or phen (in alcoholic medium), in the presence of hydrohalic acid or perchloric acid, to give cationic complexes of the formula $[\text{RhX}_2(\text{N-N})(\text{Ph}_2\text{RAs})_2]^+$. It is of interest to find that the analogous complexes of ruthenium(III) $\text{RuCl}_3(\text{Ph}_2\text{RAs})_3$ under similar conditions give neutral crystalline complexes of

composition $\text{RuCl}_3(\text{N-N})(\text{Ph}_2\text{RAs})$. It is also noticed that in the absence of HCl or HClO_4 these products are not easily isolable. Hence, it is likely that the substitution reactions are catalysed by hydrogen ions. It may be noted, here, that Ruiz-Ramirez and Stephenson[10], and Natarajan *et al.*[11] have prepared analogous complexes starting from the complexes $\text{RuX}_3\text{L}_2(\text{MeOH})$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}$) and $\text{RuCl}_3(\text{Ph}_3\text{As})_3$ respectively.

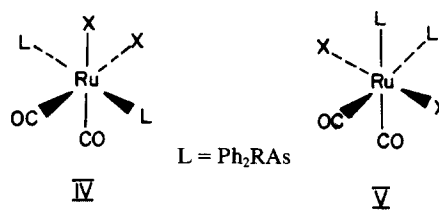
The compounds $\text{RuCl}_3(\text{N-N})(\text{Ph}_2\text{RAs})$ give non-conducting solutions in nitrobenzene and show bands due to the coordinated nitrogen ligands in the infrared. The poor solubility and paramagnetic nature of the complexes precluded measurement of their nmr spectra. The magnetic moment values (μ_{eff} , 2–2.5 B.M.; Table 1) though rather high for one unpaired electron (spin paired d^5 electron configuration in an octahedral environment) are nevertheless in the right range for complexes of ruthenium(III)[10] for which a considerable orbital contribution is expected. This is also supported by the ESR spectra, (at room temperature) which show a broad resonance signal with a 'g' value around 2.1. Assuming a *meridional* configuration (structure II)[12] for the complexes $\text{RuCl}_3(\text{Ph}_2\text{RAs})_3$ we suggest that the complexes



$\text{RuCl}_3(\text{N-N})(\text{Ph}_2\text{RAs})$ have configuration III. Further ruthenium(III) (t_{2g}^5) appears to favour the formation of neutral complexes of the above type in preference to

cationic complexes of the type formed by rhodium(III) (t_{2g}^6 electron configuration). Ruiz-Ramirez and Stephenson[10] have, however, reported recently the isolation of a ruthenium(III) cationic complex of the formula $[\text{RuCl}_2\text{bipy}(\text{Ph}_3\text{P})_2]\text{BPh}_4$ using methanol as the reaction medium. They suggest that in the polar solvent methanol, preferential replacement of halide ion, rather than Ph_3P occurs, and the resulting ruthenium(III) cation is precipitated by the bulky anion BPh_4^- .

We have also synthesised a series of dicarbonyl complexes of ruthenium(II) of stoichiometry $\text{RuX}_2(\text{CO})_2(\text{Ph}_2\text{RAs})_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Pr}, \text{Bu}$) by the addition of the arsine to the pale yellow solution obtained by passing carbon monoxide through an alcoholic solution of ruthenium halide. These compounds are non-electrolytes in nitrobenzene and show two νCO bands around 2000 cm^{-1} (Table 2) and so should have configuration IV or V in analogy with the earlier findings [6].



EXPERIMENTAL

The metal (ruthenium and rhodium) halides were supplied by Johnson Matthey Chemicals Ltd., London. The arsines, Ph_2RAs ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$) were prepared as reported elsewhere[13]. IR spectra (Nujol mulls) were recorded with a Carl Zeiss UR 10 spectrophotometer. Magnetic moments were measured with a Guoy balance using $\text{Co}[\text{Hg}(\text{CNS})_4]$ as the calibrant. Conductivity

Table 1. Physical properties and analytical data of ruthenium(III) complexes

Compound	Colour	M.p. or Dec. P. ($^{\circ}\text{C}$)	$\mu_{\text{eff}}^{\dagger}$ (B.M.)	Analytical data (%) \ddagger			
				(C)	(H)	(X)	(N)
$\text{RuCl}_3(\text{PrPh}_2\text{As})_3$	Black	186–88	2.41	52.9 (52.8)	5.1 (5.0)	10.4 (10.4)	—
$\text{RuCl}_3(\text{BuPh}_2\text{As})_3$ \S	Black	209–10	2.06	50.4 51.3 50.7 (54.1)	5.7 5.0 5.1 (5.4)	10.3 — 10.2 (10.0)	—
$\text{RuCl}_3\text{bipy}(\text{MePh}_2\text{As})$	Brickred	259–61	2.30	45.7 (45.4)	3.8 (3.5)	—	4.6 (4.6)
$\text{RuCl}_3\text{phen}(\text{MePh}_2\text{As})$	Brickred	292–94	2.00	47.3 (47.5)	3.7 (3.3)	15.9 (16.9)	4.4 (4.4)
$\text{RuCl}_3\text{bipy}(\text{EtPh}_2\text{As})$	Brickred	215–18	2.47	46.7 (46.3)	3.8 (3.7)	—	4.6 (4.5)
$\text{RuCl}_3\text{phen}(\text{EtPh}_2\text{As})$	Brickred	229–32	2.40	48.2 (48.3)	3.6 (3.6)	15.2 (16.5)	4.5 (4.3)
$\text{RuCl}_3\text{bipy}(\text{PrPh}_2\text{As})$	Brickred	229–32	2.05	47.3 (47.2)	4.0 (3.9)	—	5.0 (4.4)
$\text{RuCl}_3\text{phen}(\text{PrPh}_2\text{As})$	Brickred	258–61	2.36	49.0 (49.1)	3.8 (3.8)	—	4.6 (4.2)
$\text{RuCl}_3\text{bipy}(\text{BuPh}_2\text{As})$	Brickred	238–40	\parallel	47.6 (48.0)	4.3 (4.2)	—	4.4 (4.3)
$\text{RuCl}_3\text{phen}(\text{BuPh}_2\text{As})$	Brickred	240–42	\parallel	50.6 (49.9)	4.1 (4.0)	—	4.4 (4.2)

\dagger Values for $\text{RuCl}_3(\text{MePh}_2\text{As})_3$ and $\text{RuCl}_3(\text{EtPh}_2\text{As})_3$ are 2.34 and 2.10 B.M. respectively.

\ddagger Calculated values are in parentheses.

\S Although this compound is of low state of purity, bipy and phen derivatives made out of it give satisfactory elemental analysis.

\parallel Not measured.

Table 2. Physical properties and analytical data of ruthenium(II) complexes

Compound	Colour	M.p. or Dec.P. (°C)	Λ^\ddagger	ν_{CO} (cm^{-1})	Analytical data (%) \ddagger		
					(C)	(H)	(X)
$\text{RuCl}_2(\text{MePh}_2\text{As})_4$	Pink	174–76	§	—	54.4 (54.4)	4.5 (4.5)	5.4 (6.2)
$[\text{Ru}_2\text{Cl}_3(\text{MePh}_2\text{As})_6]\text{Cl}$	Yellow	226–28	23.6	—	51.5 (51.8)	4.5 (4.3)	—
$[\text{Ru}_2\text{Cl}_3(\text{PrPh}_2\text{As})_6]\text{Cl}$	Yellow	176–78	25.2	—	54.8 (54.6)	5.5 (5.2)	7.3 (7.2)
$[\text{Ru}_2\text{Cl}_3(\text{BuPh}_2\text{As})_6]\text{Cl}$	Yellow	174–76	28.2	—	55.7 (55.9)	5.5 (5.5)	6.5 (6.9)
$[\text{Ru}_2\text{Cl}_3(\text{MePh}_2\text{As})_6][\text{Rh}(\text{CO})_2\text{Cl}_2]$	Yellow	205–207	23.6	1981 2056	47.6 (47.9)	4.1 (3.9)	—
$[\text{Ru}_2\text{Cl}_3(\text{EtPh}_2\text{As})_6][\text{Rh}(\text{CO})_2\text{Cl}_2]$	Yellow	168–70	20.5	1986 2060	49.5 (49.5)	4.3 (4.4)	7.8 (8.5)
$[\text{Ru}_2\text{Cl}_3(\text{PrPh}_2\text{As})_6][\text{Rh}(\text{CO})_2\text{Cl}_2]$	Yellow	165–67	22.6	1980 2060	51.8 (50.8)	4.9 (4.7)	—
$[\text{Ru}_2\text{Cl}_3(\text{BuPh}_2\text{As})_6][\text{Rh}(\text{CO})_2\text{Cl}_2]$	Yellow	168–70	22.7	1980 2060	51.5 (52.2)	4.9 (5.1)	—
$\text{RuCl}_2(\text{CO})_2(\text{PrPh}_2\text{As})_2$	White	251–53	§	1993 2055	50.1 (49.8)	4.5 (4.4)	—
$\text{RuBr}_2(\text{CO})_2(\text{PrPh}_2\text{As})_2$	Pale-yellow	246–48	§	1990 2053	44.6 (44.8)	4.0 (4.1)	—
$\text{RuCl}_2(\text{CO})_2(\text{BuPh}_2\text{As})_2$	White	178–80	§	1999 2060	50.4 (51.0)	4.8 (4.8)	8.1 (8.9)
$\text{RuBr}_2(\text{CO})_2(\text{BuPh}_2\text{As})_2$	Pale-yellow	200–202	§	1983 2053	45.9 (45.9)	4.5 (4.3)	16.7 (18.0)

\ddagger Molar conductance ($\Omega^{-1} \text{cm}^2 \text{mole}^{-1}$) of $ca. 10^{-3} \text{M}$ solutions in nitrobenzene at 25°C .

\ddagger Calculated values are in parentheses.

§ Non electrolyte.

measurements were made with a Toshniwal conductivity bridge type CL 01.02. Micro-analysis for carbon, hydrogen and nitrogen, were carried out at the University of Sussex, England, and I.I.T., Kanpur. Halogen was estimated by sodium hydroxide fusion and subsequent titration by the Volhard's method. NMR spectra were recorded with a Varian T-60 instrument using CDCl_3 as solvent and TMS as internal reference.

Trichloro tris(tertiary arsine) ruthenium(III) compounds:
 $\text{RuCl}_3(\text{Ph}_2\text{RAs})_3$

To an ethanol (20 ml) solution of ruthenium trichloride (1 mmole) containing concentrated hydrochloric acid (1.5 ml), the arsine (3 mmole) in ethanol (30 ml) was added, and the mixture was refluxed on a steam-bath for about 2 hr. The compound separated as shining black crystals from the dark solution. It was filtered, washed successively with water and alcohol, and dried *in vacuo*.

Trichloro 2,2'-bipyridyl(or o-phenanthroline) tertiary arsine ruthenium(III) compounds: $\text{RuCl}_3(\text{N-N})(\text{Ph}_2\text{RAs})$ (N-N = bipy, phen)

To an ethanol (50 ml) suspension of $\text{RuCl}_3(\text{Ph}_2\text{RAs})_3$ (1 mmole), bipy or phen (1 mmole) was added followed by HClO_4 or HCl (1.5 ml). The mixture was refluxed on a steam-bath for about 5 hr. and the brick red crystalline solid that separated (in some cases on concentration of the resulting dark red solution) was filtered, washed successively with water and ether, and dried *in vacuo*.

Dichloro tetrakis(diphenyl methyl arsine) ruthenium(II):
 $\text{RuCl}_2(\text{Ph}_2\text{MeAs})_4$

To an ethanolic (20 ml) solution of ruthenium trichloride (1 mmole), diphenyl methyl arsine (8 mmole) in ethanol (15 ml) was added and the mixture was refluxed on a steam-bath for about 12 hr. The shining pink crystals that separated were washed with water, ethanol and dried *in vacuo*.

Tri- μ -chloro hexakis(tertiary arsine) diruthenium(II) chloride compounds: $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6]\text{Cl}$

Ruthenium trichloride (1 mmole) and the tertiary arsine (8 mmole) were taken in ethanol (130 ml), and the mixture was refluxed on a steam-bath for about 50 hr. The solution was filtered and the filtrate was concentrated under reduced pressure to nearly 3 ml. To this, on the dropwise addition of water, the required compound got separated as yellow powder. It was filtered, washed with ether (hexane for Ph_2PrAs compound) and water, and dried *in vacuo*.

Tri- μ -chloro hexakis(tertiary arsine) diruthenium(II) dichloro dicarbonyl rhodate(I) compounds: $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6][\text{RhCl}_2(\text{CO})_2]$

Carbon monoxide was passed into a hot alcoholic solution (5 ml) of rhodium trichloride (0.22 mmole) till the solution turned pale yellow. The solution was cooled to about 5°C and to this was added an alcoholic solution (5 ml) of $[\text{Ru}_2\text{Cl}_3(\text{Ph}_2\text{RAs})_6]\text{Cl}$ (0.2 mmole). The yellow or orange crystalline solid that separated was washed successively with water and ether, and dried *in vacuo*.

Dichloro dicarbonyl bis(tertiary arsine) ruthenium(II) compounds:
 $\text{RuX}_2(\text{CO})_2(\text{Ph}_2\text{RAs})_2$ (X = Cl, Br; R = Pr, Bu)

Carbon monoxide was passed into a hot methoxyethanol solution (10 ml) of ruthenium halide (0.3 mole) till the solution turned pale yellow (about 3 hr). To this, the tertiary arsine (0.6 mmole) was added, and the solution was refluxed for another 10 min under CO atmosphere. Dropwise addition of water produced the carbonyl complex as shining white (or pale yellow) crystals. The crystals were washed with water and alcohol, and dried *in vacuo*.

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